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SYNTHESIS OF ELASTOMERS CONTAINING Si-N BONDS IN THE MAIN CHAIN

SUMMARY REPORT NO. 2
29 June 1962 - 30 June 1963

Contract No. DA-23-072-ORD-1687
Dept. of Army Project No. 593-32-002

M.R.I. Project No. 2531-C

For

Rock Island Arsenal
Rock Island, Illinois

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by

L. W. Breed
R. L. Elliott

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PREFACE

This report was prepared by Midwest Research Institute under U. S. Army Contract No. DA-23-072-ORD-1687. The work was administered under the direction of Rock Island Arsenal, Rock Island, Illinois, with Mr. Z. T. Ossefort acting as Project Officer.

This report covers work conducted from 29 June 1962 - 30 June 1963.

Project personnel were Messrs. Richard Elliott and L. W. Breed, who acted as project leader.

Approved for:

MIDWEST RESEARCH INSTITUTE

F. V. Morriss, Director
Chemistry Division

15 July 1963

ABSTRACT

Polymers with intrinsic viscosities in toluene of up to 1.80 have been prepared by the condensation of silazanes with organic diols. Elemental analyses and infrared spectra are reported for several of the polymers, and their hydrolytic and thermal stability are discussed. The preparations of a polymer from p-phenylenebis(dimethylmethylaminosilane), and the reactions of cyclic silazanes under the influence of acids and bases are also described.

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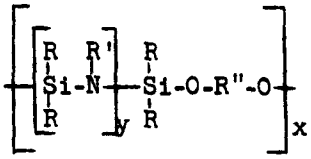
SUMMARY

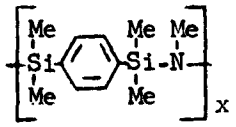
A series of new polymers has been prepared by the condensation of linear or cyclic silazanes with organic diols to yield materials with the following structure:



y = 1 or 2

These polymers have been characterized by elemental analysis and infrared spectra. Screening experiments were employed to determine the most satisfactory silazanes and diols for the polymerization reaction. Although polymers with intrinsic viscosities in toluene up to 1.60 have been obtained from bisphenol "A" and hexamethylcyclotrisilazane, hydrolytic stability can be considerably improved and equally high intrinsic viscosities obtained when bisphenol "A" and nonamethylcyclotrisilazane are used. Thermal decomposition of these polymers occurs above 450° C on thermogravimetric analysis at a heating rate of 3°/min under nitrogen.

A new silazane polymer containing phenylene-linked silicon atoms has also been prepared, but the polymer had a relatively low molecular weight.



In addition, the possibility of catalytically interconverting cyclic and linear silazanes was investigated as a route to silicon-nitrogen polymers. Conversions to nonvolatile products by this procedure were generally low.

A method for determining the hydrolytic stability of silicon-nitrogen polymers was developed and applied to representative new polymers. On the basis of the experimental results, it is shown that improved hydrolytic stability in silicon-nitrogen polymers is obtained from structural modifications in which the Si_2NMe, Si_3N, or Si_2NRNSi_2 group is substituted for the Si_2NH group.

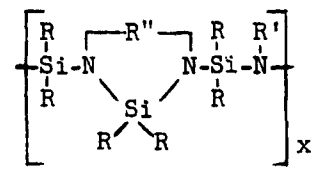
Details of the synthesis of monomers and intermediates are given. Attempts to prepare N,N'-bis(chlorodimethylsilyl)-N"-trimethylsilylhexamethylcyclotrisilazane as a polymer intermediate have been unsuccessful.

I. INTRODUCTION

The work described in this report is a continuation of the work reported in Summary Report No. 1, July 1962. The objective has been to develop synthesis methods for thermally and hydrolytically stable elastomers based on chains containing silicon atoms bonded directly to nitrogen, and to conduct preliminary screening of the materials obtained.

In the silicon-nitrogen series, experimental approaches to elastomers may be conveniently divided into three phases: (A) Linear, thermally-stable polymers with higher molecular weights than have heretofore been reported must be prepared; (B) the polymer, once prepared, must be suitably modified to achieve hydrolytic stability; and (C) the thermally and hydrolytically stable polymer must be converted by suitable means to a material with elastomeric character.

In Summary Report No. 1, new polymers containing alternately ordered silicon and nitrogen atoms in the main chain were reported.



A study of the variables associated with monomer composition and polymerization conditions failed to provide a method for preparing polymers of this kind with molecular weights greater than about 15,000. Some work on the thermal decompositions of $R_2Si(NHR')_2$ compounds was also reported.

The primary emphasis in the work covered in this report and in Summary Report No. 1 has been the synthesis of high molecular weight silicon-nitrogen polymers. In addition, some work has been concerned with improved hydrolytic stability. Rock Island Arsenal has studied the conversion of several of the higher molecular weight polymers to elastomers; however, that work is not covered in this report.

II. POLYMERS FROM SILAZANES AND DIOLS

It has been found that polymers can be prepared by heating cyclic or linear silazanes with dihydroxy compounds. The following are typical reactions.

$$(Me_2SiNH)_3 + \underline{m}\text{-}C_6H_4(OH)_2 \longrightarrow \left[O\text{-}\underline{m}\text{-}C_6H_4\text{-}O\text{-}SiMe_2NHSiMe_2NHSiMe_2\right]_n + NH_3$$

$$MeNHSiMe_2NMeSiMe_2NHMe + HOCH_2\text{-}\underline{p}\text{-}C_6H_4\text{-}CH_2OH \longrightarrow$$

$$\left[O\text{-}CH_2\text{-}\underline{p}\text{-}C_6H_4\text{-}CH_2\text{-}O\text{-}SiMe_2NMeSiMe_2\right]_n + NH_3$$

The stoichiometry in this polymerization reaction is not critical. The initial step in the reaction may be postulated as the cleavage of the silazane ring, and the second step as the condensation of the free amino group resulting from the cleavage with an additional molecule of the diol. The free

$$(SiMe_2NH)_3 + HOROH \longrightarrow HOROSi(NHSiMe_2)_2NH_2$$

$$HOROSi(NHSiMe_2)_2NH_2 + HOROH \longrightarrow HOROSi(NHSiMe_2)_2OROH$$

hydroxyl groups may then cleave additional silazane rings. If the silazane is present in excess the silyl amine group, which can condense to form the silazane linkage between two polymer molecules, will be present as the end group. If the diol is present in excess, sites along the polymer chain will cleave and recombine in a manner similar to the initial ring cleavage. The large difference in the acidity of the hydrolyl group and silylamine group allows the polymerization reaction to predominate with negligible contributions of rearrangement reactions.

In the screening of monomer compositions, the quantity of ammonia or amine evolved during the reaction was determined, and the degree of polymerization of the final polymer was assessed in terms of intrinsic viscosities of polymer solutions. Detailed descriptions of these experiments are given in Table I.

In general, the most satisfactory procedure employed a solution of equimolar quantities of the diol and silazane in toluene solution (for example,

TABLE I

POLYMERS FROM SILAZANES AND ORGANIC DIOLS

Diol or Diamine	Solvent	Polymerization Temperature °C	Amine Evolved (%)	Polymer Yield (%)	$[\eta]$ in Toluene	Comments
Hexamethylcyclotrisilazane with:						
Resorcinol[a]	Toluene	114°/24 hr	92	98	0.79	From pyridine $[\eta]$ = 0.45
Bisphenol "A"[b]	Toluene	125°/2 hr	89	103	1.60	Additional solvent was added during polymerization (20 ml.)
Hydroquinone[c]	Toluene	115-20°/24 hr	95	98	0.33	
Catechol[d]	Toluene	115-20°/24 hr	-	Trace	-	
4,4'-Oxydiphenol[e]	Toluene	117°/24 hr	87	100	0.55	
4,4'-Biphenol[f]	Toluene	130°/24 hr	97	-	0.72	
1,4-Benzenedimethanol[g]	Toluene	115-20°/24 hr	-	100	0.45	
1,4-Cyclohexanedimethanol[h]	Toluene	115°/24 hr	85	98	0.79	
Hydrogenated bisphenol "A"[i]	Toluene	121°/24 hr	68	83	0.06	
2,2,4,4-Tetramethyl-1,3-cyclobutanediol[j]	Toluene	118-155°/70 hr	81	92	0.26	
4,4'-Bis(hydroxymethyl)diphenyl ether[k]	Toluene	115-19°/48 hr	64	86	0.10	
Novalac[l]	Toluene	110°/23 hr	163	-	-	Insoluble, infusable polymer
Diphenylsilanediol[m]	Toluene	115-20°/24 hr	-	97	<0.075	
p-Phenylenediamine[n]	Toluene	117°/24 hr	113	90	0.04	
4,4'-Methylenedianiline	Toluene	115°/24 hr	134	94	<0.05	$[\eta]$ = 0.14 with no solvent at 195° in the presence of ammonium sulfate
Nonamethylcyclotrisilazane with:						
Resorcinol	Toluene	115-200°/22 hr	98	100	0.21	From pyridine at 117° $[\eta]$ = 0.39
Bisphenol "A"	Toluene	112-120°/24 hr	100	-	1.85	Polymerization reaction was very sensitive to silazane purity
1,3-Bis(methylamino)pentamethyldisilazane with:						
1,4-Benzenedimethanol	None	190-200°/24 hr	90	84	0.39	
4,4'-Biphenol	Toluene	115°/24 hr	95	-	0.43	
Bisphenol "A"	Toluene	130°/24 hr	85	89	0.76	
Resorcinol	None	220°/24 hr	89	98	0.23	
Octamethylcyclotrisilazane with:						
Resorcinol	Toluene	115-20°/24 hr	-	68	0.56	In reactions without solvent, difficulty was encountered in the sublimation of the silazane
Hydroquinone	Toluene	115-20°/24 hr	91	-	0.23	
1,4-Benzenedimethanol	Toluene	115-20°/24 hr	92	-	0.42	
Diphenylsilanediol	Toluene	115-20°/24 hr	82	68	0.19	
4,4'-Methylenedianiline	None	194°/24 hr	78	-	0.07	
1,3,5-Triphenylhexamethylcyclotrisilazane with:						
Resorcinol	None	115-80°/24 hr	-	83	0.03	
1,3-Bis(aminodimethylsilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane with:						
Resorcinol	Toluene	117°/24 hr	-	95	0.04	
N-trimethylsilylhexamethylcyclotrisilazane with:						
Bisphenol "A"	Toluene	113-122°/90 hr	-	93	0.09	The intrinsic viscosity was not increased on additional heating of the polymer or by using ammonium sulfate as a catalyst in the reaction
N,N'-Bis(trimethylsilyl)hexamethylcyclotrisilazane with:						
Resorcinol	Toluene	115°/24 hr	98	101	<0.03	The intrinsic viscosity was not increased on additional heating of the polymer at 200°
Bisphenol "A"	Toluene	126-36°/24 hr	95	72	0.03	
Bisphenol "A"[o]	Toluene	112°/24 hr	98	-	0.66	From pyridine $[\eta]$ = 0.23

[a] Fisher, certified. [b] Eastman 4,4'-isopropylidenediphenol, m.p. 155-56°. [c] Fisher, purified. [d] Fisher, certified, resublimed. [e] Eastman, m.p. 186-7°. [f] Eastman, m.p. 276-8°. [g] Aldrich. [h] Eastman, redistilled at 137-40°/2 mm. [i] Monsanto. [j] Eastman, m.p. 125-35°. [k] Dow, recrystallized three times from toluene and once from isopropyl alcohol. [l] Dow, a diphenyl oxide modified Novalac. [m] Dow Corning, technical. [n] Recrystallized from ethanol and dried in vacuum. [o] Catalyzed with 1 wt. per cent $(NH_4)_2SO_4$.

0.02 mole of hexamethylcyclotrisilazane and 0.02 mole of resorcinol in 10 ml. of toluene). The reactants were heated at about 115° (reflux) under nitrogen for about 24 hr., and the evolved ammonia or amine was collected in an acid trap for subsequent back titration. The polymer was devolatilized under vacuum up to 100°C.

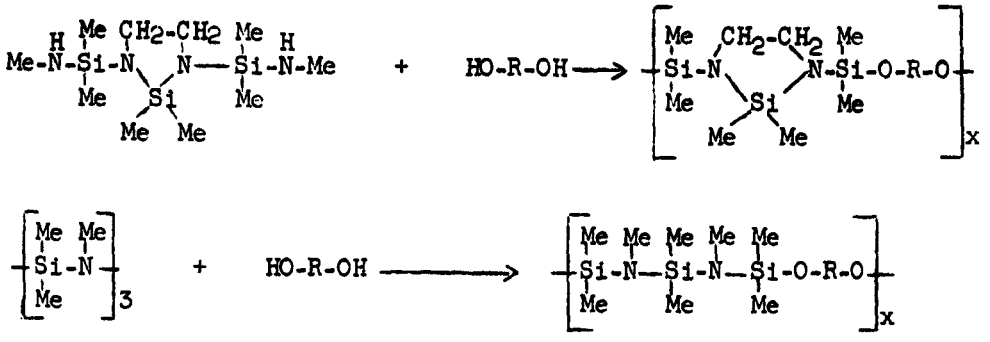
Variations in experimental conditions appeared to have less influence on the nature of the product than changes in the degree of purity of the monomers. In some experiments, no solvent was used and the reactants were heated at about 200° for 24 hr. In others, the solvent was distilled out during an initial heating period, and the temperature of the mixture was raised to 200° for the remainder of the polymerization. Other reaction solvents were also employed, particularly pyridine and xylene, the latter affording a higher reaction temperature, but the molecular weights of the resulting polymers were not significantly raised. Improvements were obtained in some but not all polymers when catalytic quantities of ammonium sulfate were added to the reaction mixtures. Additional heating of some of the finished polymers under vacuum failed to increase the molecular weight.

A large number of experiments were carried out in order to screen monomers for their potential utility in the silazane-diol reaction. The relative molecular weight achieved with a particular combination of reactants was estimated from the intrinsic viscosity of the corresponding polymer. The particular experiments giving the highest molecular weight polymers for each set of monomers are reported in Table I.

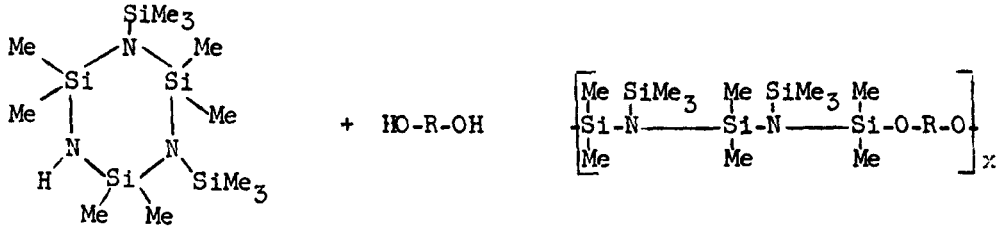
Many aromatic diols gave satisfactory polymers, but those from bisphenol "A" exhibited the highest intrinsic viscosity. Other satisfactory diols include resorcinol, 4,4'-oxydiphenol, 4,4'-biphenol, 1,4-benzenedimethanol, and 1,4-cyclohexanedimethanol.

Because hexamethylcyclotrisilazane is readily available, it was most frequently employed as the silazane in the screening of diols. Octamethylcyclotetrasilazane, a solid, was not satisfactory because it sublimed from the polymerization mixtures.

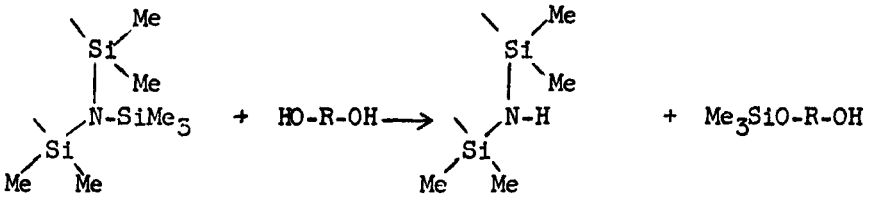
Improved thermal and hydrolytic stability can be expected when the structure of the silazane monomer is selected to produce polymers in which the nitrogen atoms are entirely substituted by alkyl or silyl groups. Polymers with N-alkyl substituents were satisfactorily prepared from 1,3-bis(methylamino)-pentamethyldisilazane and 1,3-bis(dimethylmethylaminosilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane, but higher molecular weight polymers were obtained from nonamethylcyclotrisilazane.



Of considerable interest is the polymer that can be expected from N,N'-bis(trimethylsilyl)hexamethylcyclotrisilazane.



High molecular weight polymers have not yet been obtained either from this monomer or from N-trimethylsilylhexamethylcyclotrisilazane. Failure to effect a satisfactory condensation reaction apparently can be attributed to the stabilization of the cyclotrisilazane achieved in the N-trimethylsilylated derivatives. Evidence from infrared spectra support the conclusion that a possible side reaction leading to the formation of trimethylsilyl derivatives of the diols, a chain stopper, was not important. The infrared spectrum of a low polymer from



N-trimethylsilylhexamethylcyclotrisilazane and bisphenol "A" (see Fig. 9, p. 15) contained a strong band at 1030 cm.$^{-1}$ indicating the NSi_3 group remained intact during the reaction. The intensity of the NH absorption was considerably less in the polymer than in the monomer; (see Fig. 10, p. 24), therefore, the polymerization reaction apparently proceeded in the proposed manner.

III. PHENYLENE-LINKED SILAZANE POLYMERS

The possibility of preparing polymers with the following structure was examined:

Although the amino derivative (R = H) is the monomer of choice for obtaining high molecular weight polymers, the pure compound could not be prepared. The methylamine derivative, however, was isolated and used in a polymerization reaction. When this monomer was heated in an equal volume of xylene at 137°C for 24 hr., a low polymer (η = 0.19) was obtained. This polymer exhibited reasonably good hydrolytic stability (see Fig. 8, p. 14).

IV. POLYMER PROPERTIES AND CHARACTERIZATION

The polymers ranged in appearance from viscous, tacky oils to rubbery gums, and in a few examples, waxy solids. Several of the materials could be drawn into long fibers or cast as films. Since the polymers were soluble in nonpolar solvents and gave a clear melt, it may be assumed that their structures were essentially linear.

1. Solution viscosity and molecular weight: The viscosity data shown in Table I are indicative of the relative molecular weight of the various polymers. Absolute values for molecular weight were not determined in this laboratory.[1]

Variation in intrinsic viscosities of polymers in different solvents reflected changes in polymer configuration in each solvent. A bisphenol "A" - hexamethylcyclotrisilazane condensation product, which had an intrinsic viscosity of 1.61 in toluene, exhibited intrinsic viscosities of 1.15 in perchloroethylene, and 1.07 in cyclohexane. The intrinsic viscosity of a lower molecular weight polymer from bisphenol "A" and nonamethylcyclotrisilazane changed from 0.84 in toluene to 0.73 in perchloroethylene.

2. Thermal stability: New polymers were screened for thermal stability by means of thermogravimetric analysis at a heating rate of 3°/min

under nitrogen. The results of these tests are reported in Figs. 1 and 2. Similar results for two commercial silicone rubber gums are also reported for comparison in Fig. 3.

The stability of the polymers appears to depend chiefly on the identity of the diol used in the polymerization reaction, the most stable materials being those derived from bisphenol "A" and 4,4'-biphenol. The more stable polymers gave thermograms with a characteristic knee in the vicinity of 450°C. A most interesting characteristic of these curves is the percentage of weight retention above the thermal decomposition temperature of the polymer. Unlike conventional silicone gums, these materials form a significant amount of non-volatile residue.

Several of the polymers show some tailing-off in the room temperature to 400° range. This effect, particularly noticeable in the bisphenol "A" - hexamethylcyclotrisilazane polymer, can probably be attributed to retained solvent in the polymer sample, but may also be due to some additional curing of the polymer.

A thermogram is also included to show the thermal stability of a radiation-cured bisphenol "A" - hexamethylcyclotrisilazane polymer containing some vinyl groups. The thermogram for this sample, which was cured at the 20 megarads level, did not differ greatly from the thermograms of samples cured at 5, 10, and 15 megarads.

3. Hydrolytic stability: In order to assess the effect of monomeric composition on the hydrolytic stability of polymers, it was necessary to develop a procedure capable of determining the relative stability of polymers against hydrolysis under controlled conditions. Of the methods described in the literature for following the reaction rates of systems containing silazanes or silylamines, the procedure used by Pike[2] for determining the kinetics of the reaction between silazanes and silanols appeared to be the most attractive. In this procedure, ammonia formed in the reaction was swept from the system with nitrogen and absorbed in a boric acid solution which was later titrated with dilute hydrochloric acid.

It was found that Pike's procedure could be successfully applied to differentiate the relative rates of reaction of monomeric silazanes with water. However, ammonia evolution was too slow to provide the needed differentiation within a reasonable length of time when polymers were hydrolyzed under these conditions. Also, because several hours were required to dissolve polymers in the solvent, difficulties in maintaining anhydrous solutions introduced erratic results. Higher reaction temperatures failed to increase the reaction rate sufficiently to give the needed differentiation between hydrolytic stabilities.

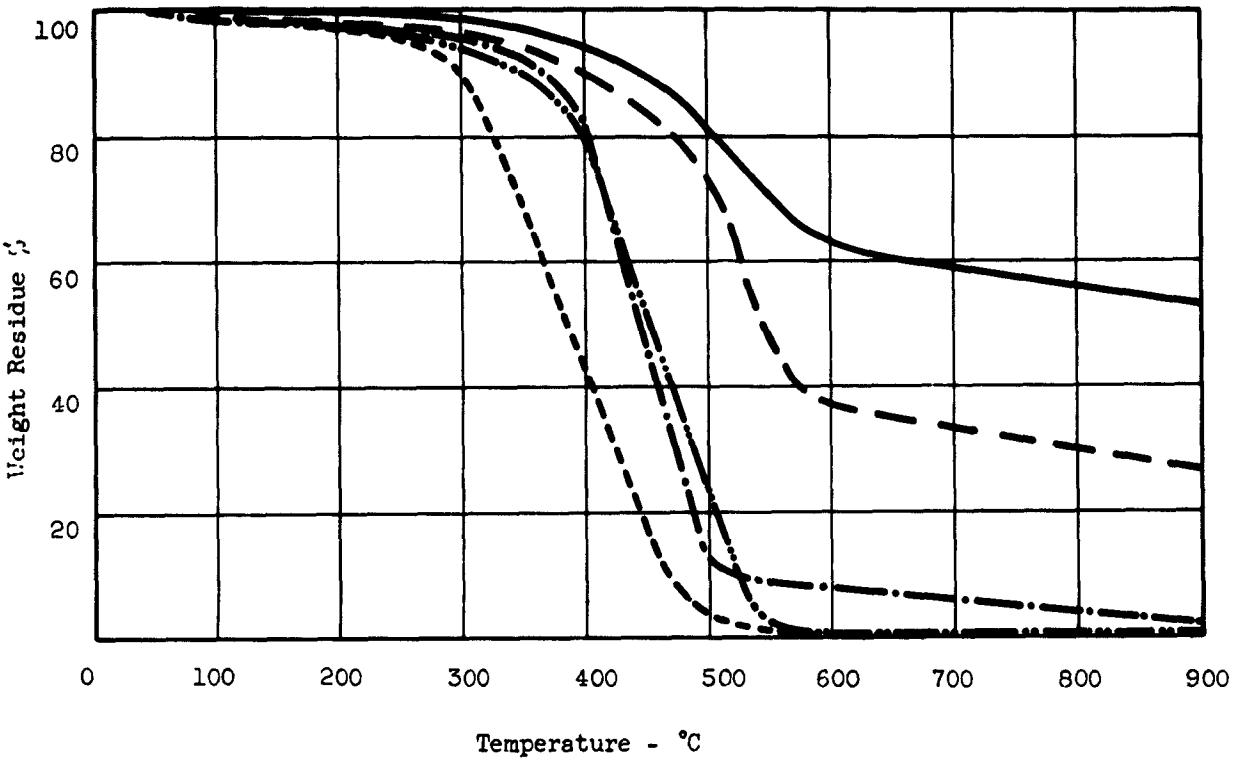
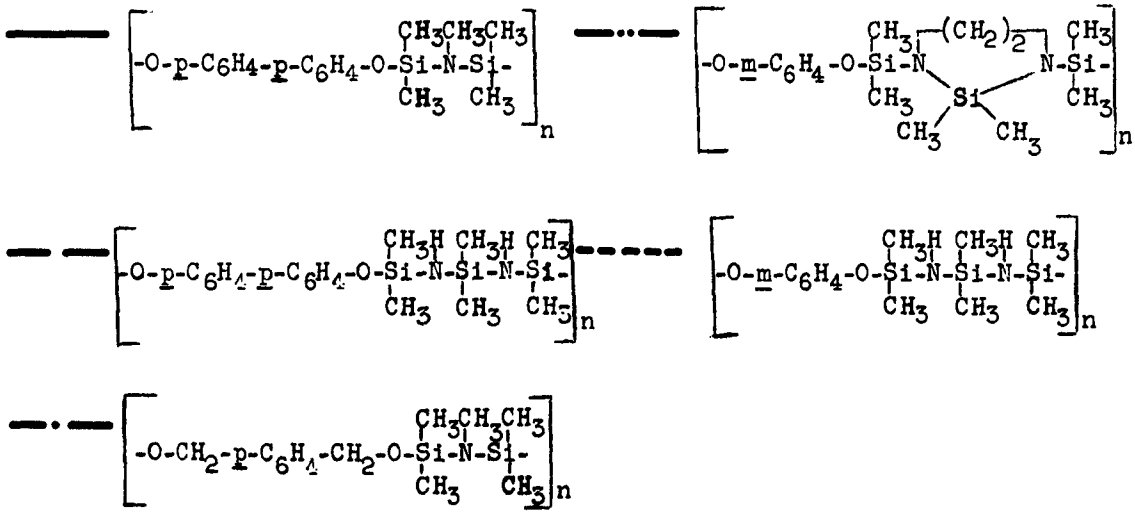


Fig. 1 - Thermogravimetric Analyses of Experimental Polymers



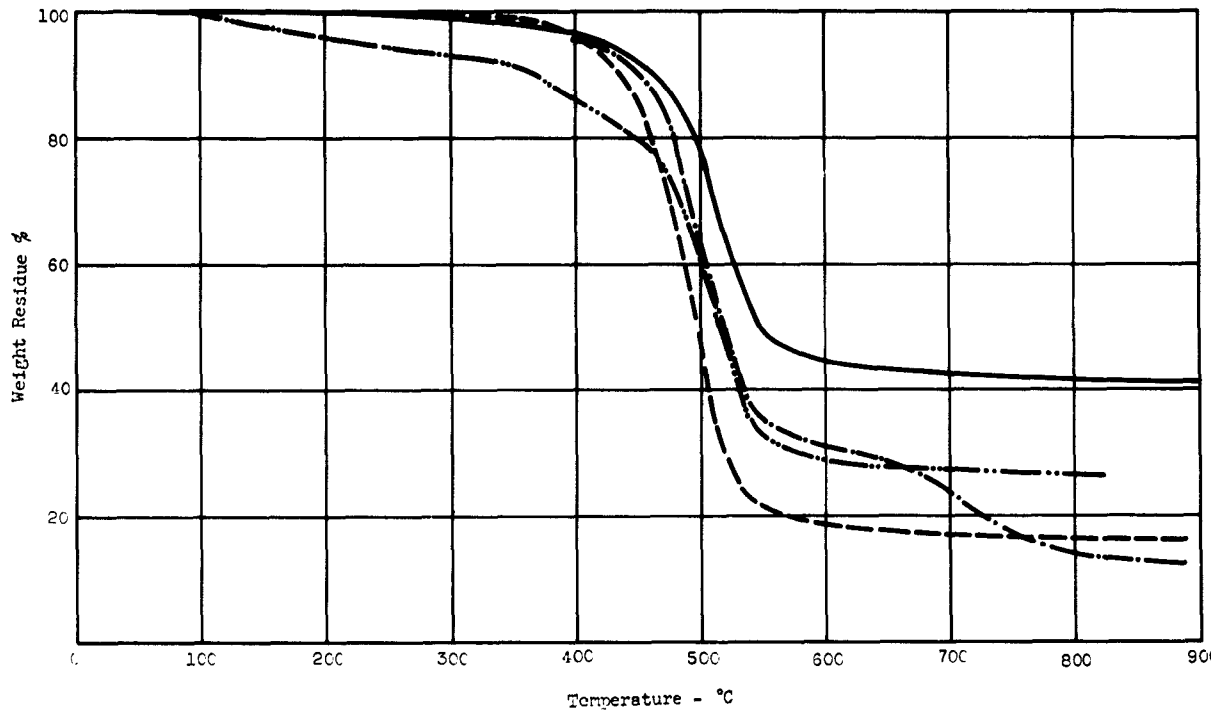
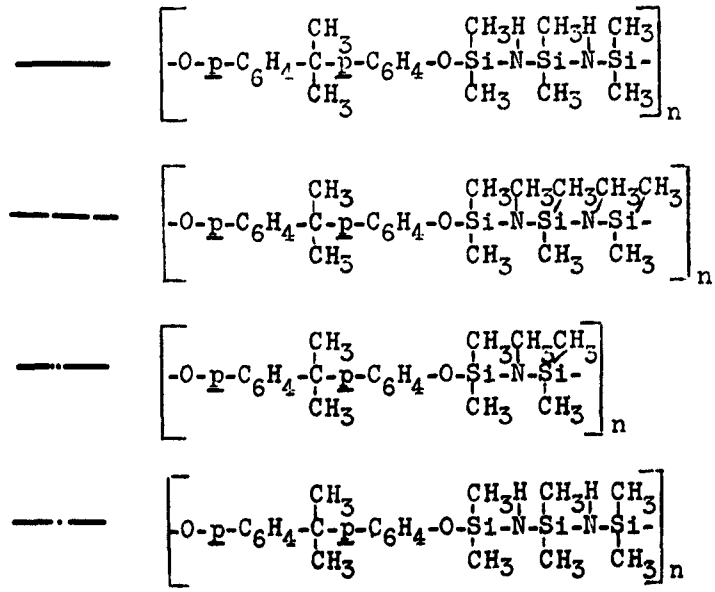


Fig. 2 - Thermogravimetric Analyses of Experimental Polymers



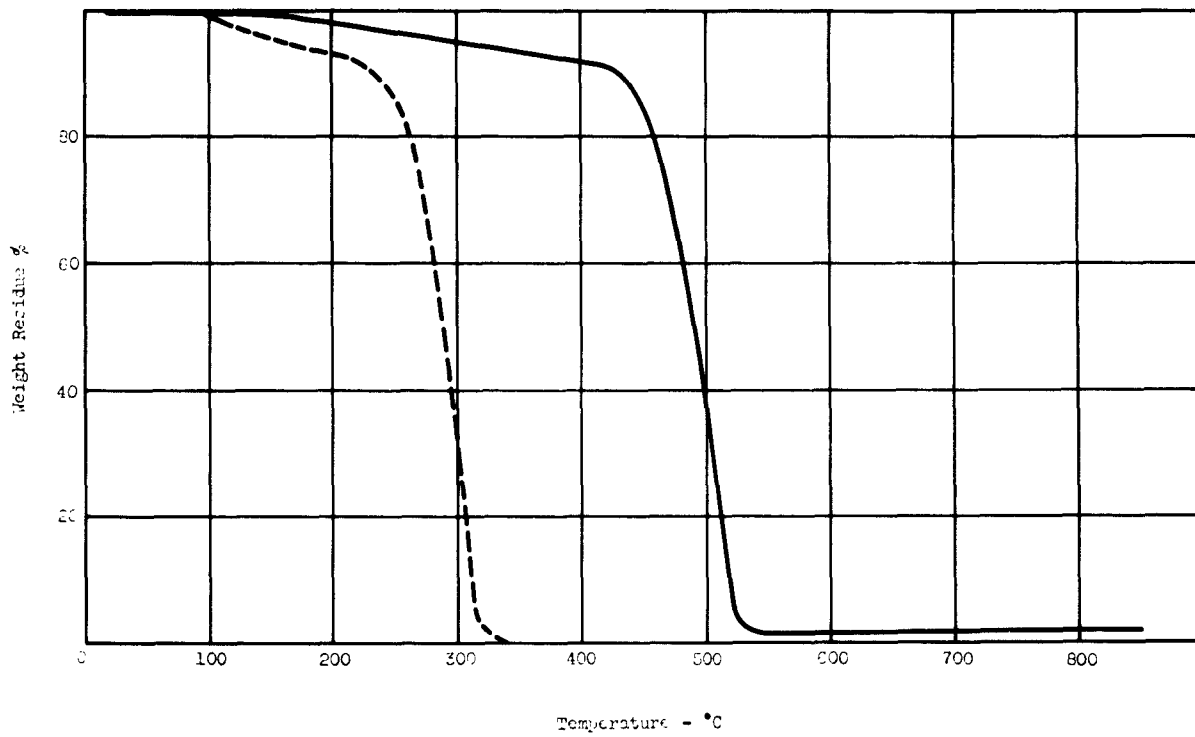


Fig. 3 - Thermogravimetric Analyses of Silicone Gums

——— Commercial methyl phenyl silicone gum

— — — Commercial dimethyl silicone gum

It was found that these difficulties could be overcome if a homogeneous mixture of toluene and wet methanol was used as the solvent for the hydrolysis. The solutions were heated at 65° and the evolved ammonia was collected and determined in the manner described previously. The results of applying this procedure to a series of polymers are summarized in Figs. 4, 5, 6, 7, and 8.

In comparing the relative rates of hydrolysis of the monomers and polymers, marked increase in the hydrolytic stability can be observed in materials in which the Si_2NH group is absent. This improvement can be effected by substituting the structures, Si_2NMe, Si_3N, or Si_2NRNSi_2. Changes in identity of the diol does not affect the hydrolytic stability of the polymer significantly, but polymers from nonamethylcyclotrisilazane and 1,5-bis(methylamino)-pentamethyldisilazane were all more hydrolytically stable. The importance of nitrogen substitution in achieving hydrolytic stability is strikingly emphasized in the polymers from the silylated derivatives of hexamethylcyclotrisilazane. The polymer from N-trimethylsilylhexamethylcyclotrisilazane, which contains one NH group per repeating unit was only slightly more hydrolytically stable than the polymer from hexamethylcyclotrisilazane (two NH groups per repeating unit). On the other hand a marked increase in hydrolytic stability was observed when N,N'-bis(trimethylsilyl)hexamethylcyclotrisilazane was employed in the polymer to give a material containing no NH groups.

The polymer based on the thermal polymerization of p-phenylenebis-(methylaminodimethylsilane), and 1,3-bis(dimethylmethylaminosilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane,[3] which contained no free Si_2NH groups, also showed a high degree of hydrolytic stability.

4. Infrared spectra: The spectra of polymers, prepared from bisphenol "A" and three silazanes are given in Fig. 9. The qualitative similarity of these spectra can be readily observed. Notable differences are the 3400 $cm.^{-1}$ band (NH), present in the polymer from hexamethylcyclotrisilazane but absent or weak in the polymers from nonamethylcyclotrisilazane and N-trimethylsilyl-hexamethylcyclotrisilazane, and the 1025 $cm.^{-1}$ band (N_3Si), present only in the polymer from N-trimethylsilylhexamethylcyclotrisilazane.

5. Elemental analysis: Analyses for elements have been obtained for three of the polymers. The results of these analyses, which are reported in Table II, are in good agreement with the calculated values.

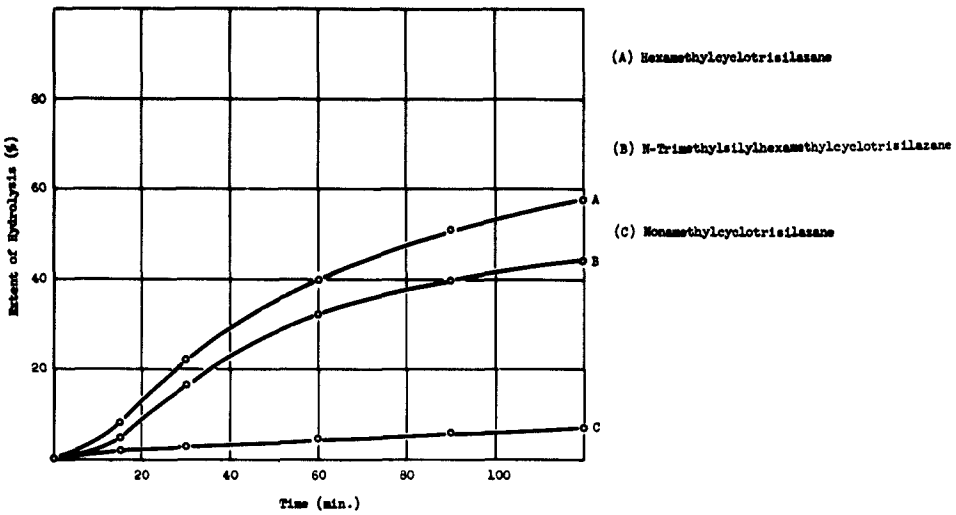


Fig. 4 - Hydrolytic Stability of Monomers

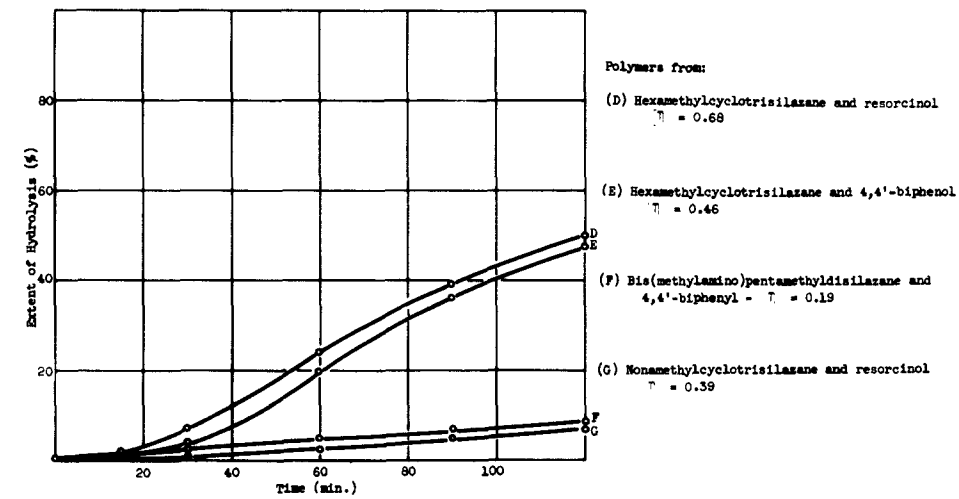


Fig. 5 - Hydrolytic Stability of Polymers

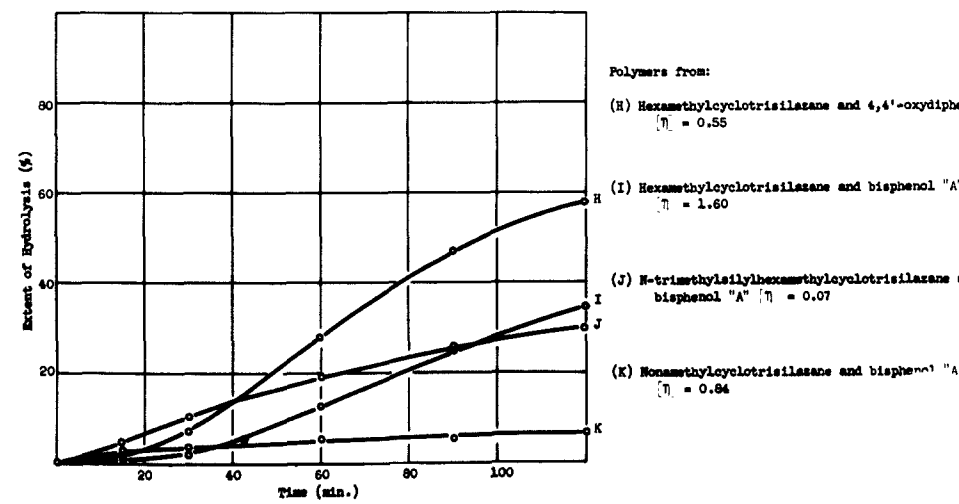


Fig. 6 - Hydrolytic Stability of Polymers

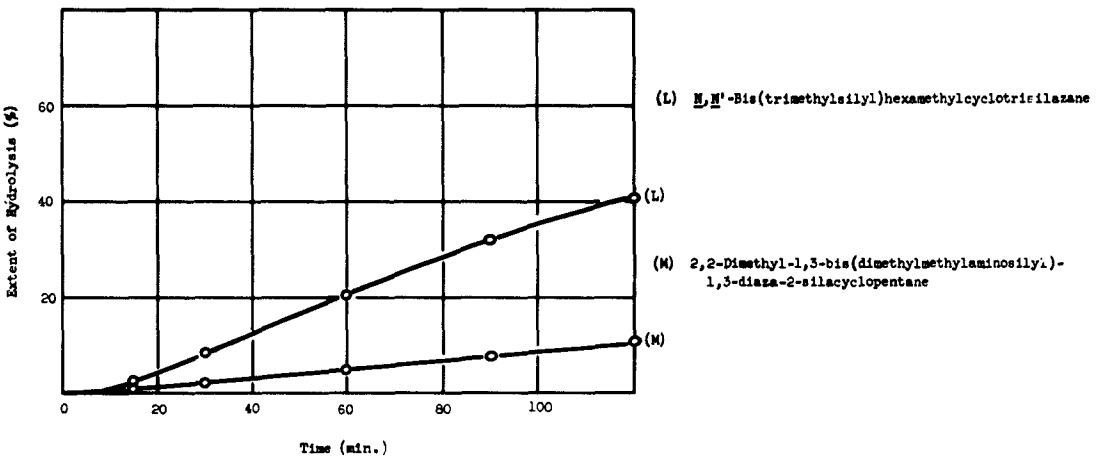


Fig. 7 - Hydrolytic Stability of Monomers

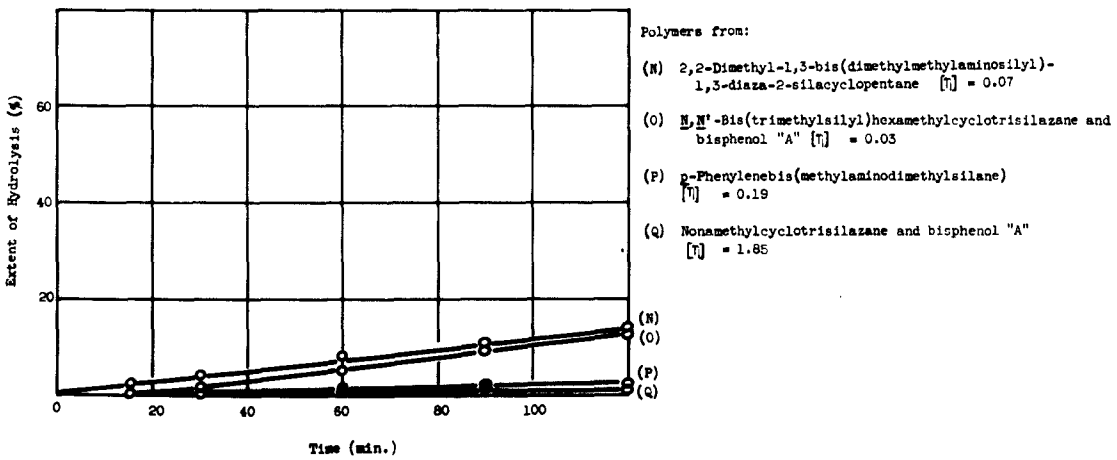
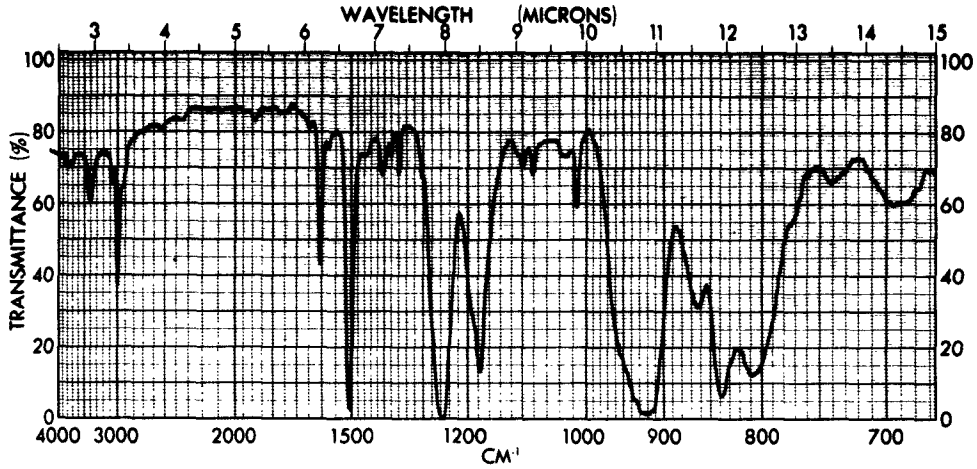
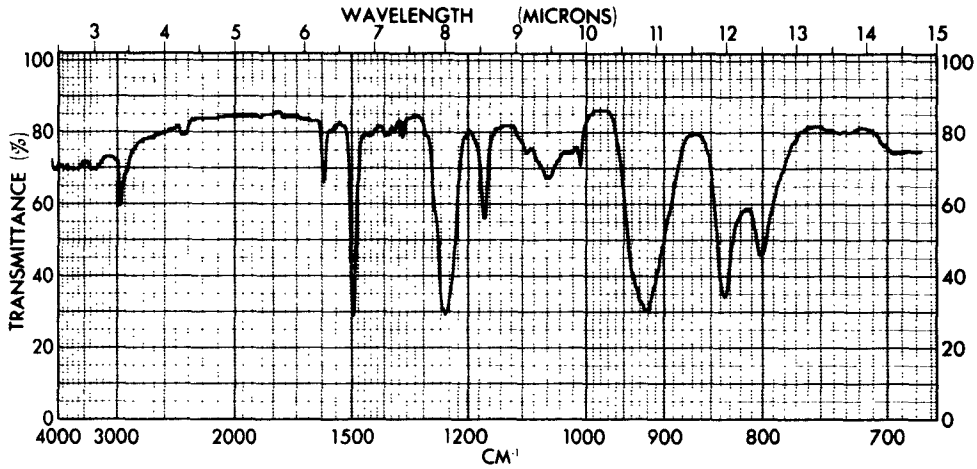


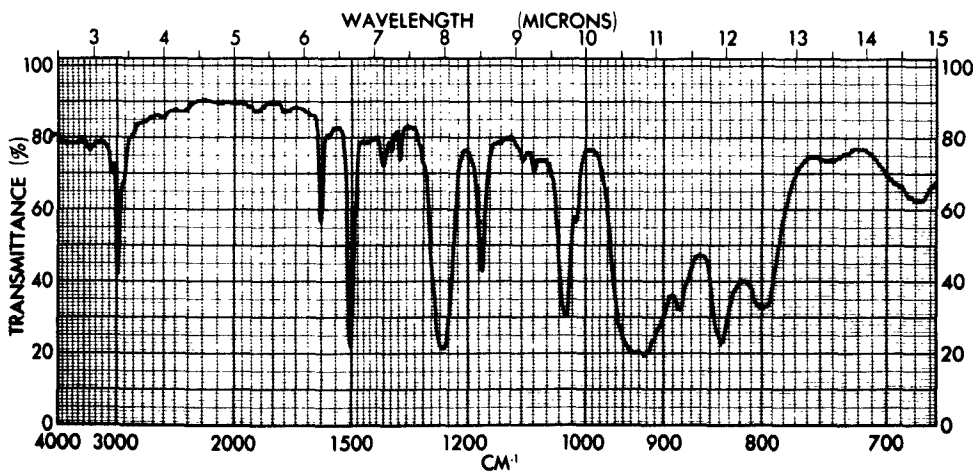
Fig. 8 - Hydrolytic Stability of Polymers



Hexamethylcyclotrisilazane and bisphenol "A"



Nonamethylcyclotrisilazane



N-Trimethylsilylhexamethylcyclotrisilazane

Fig. 9 - Infrared Spectra of Polymers

TABLE II

ELEMENTAL ANALYSES OF POLYMERS

Polymer from:	$[\eta]$ (Toluene)	Calcd. for:	Elemental Analyses							
			C		H		N		Si	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Hexamethylcyclotrisilazane and resorcinol	0.72	$C_{12}H_{24}N_2O_2Si_3$	46.10	47.82	7.74	7.59	8.96	8.71	29.96	26.11
Hexamethylcyclotrisilazane and 1,4-benzenedimethanol	0.45	$C_{14}H_{28}N_2O_2Si_3$	49.36	49.62	8.28	8.22	8.23	7.83	24.74	24.22
Hexamethylcyclotrisilazane and bisphenol "A"	1.60	$C_{21}H_{34}N_2O_2Si_3$	58.55	58.77	7.96	7.72	6.50	6.35	19.56	19.36

V. REACTIONS OF CYCLIC SILAZANES UNDER THE INFLUENCE OF ACIDS AND BASES

In view of certain recent publications, the possibility of catalytically interconverting silazane structure has also been considered.[4,5,6]

$$(R_2SiNR')_n \longrightarrow (R_2SiNR')_{n'}$$

Such a route to silicon-nitrogen polymers is attractive because of the known interconvertibility of cyclic and linear siloxanes. In a series of experiments, octamethylcyclotrisilazane was treated with a series of acid and basic catalysts under various conditions and the products were examined. The results chiefly emphasized the extreme stability of small ring silicon-nitrogen compounds.

Octamethylcyclotetrasilazane was quantitatively recovered unchanged when it was stirred with either an acid catalyst (ammonium nitrate) or a basic catalyst (sodium amide) in liquid ammonia for several hours. Concentrated aqueous ammonia at room temperature for 3 hr. also failed to affect the tetramer. When octamethylcyclotetrasilazane was refluxed in toluene or xylene in the presence of acid catalysts such as ammonium sulfate or p-toluenesulfonic acid for several days, very little change in the tetramer was observed.

In a second group of experiments, the tetramer was heated at 175° in the presence of several anhydrous Lewis acid catalysts. No attempt was made to determine ammonia evolved during these reactions, but there was no evidence of significant ammonia formation. Zinc chloride, stannic chloride and ammonium chloride did not affect octamethylcyclotetrasilazane. When aluminum chloride or ferric chloride were used as catalysts, however, 20-50 per cent conversion of octamethylcyclotetrasilazane to hexamethylcyclotrisilazane was observed, and 10-50 per cent of the starting materials was converted to nondistillable residues. Unchanged tetramer also remained in the reaction product. Octamethylcyclotetrasilazane, heated in the presence of titanium tetrachloride, antimony pentachloride, antimony trichloride, or ammonium bromide at 175°, also gave mixtures containing the trimer, tetramer, and undistillable residues.

It is apparent that in the presence of acids at 175° a randomization of the silazane system can occur, and that both the trimer and tetramer can be expected as products. Speculation on the nature of the undistillable residues, which were obtained in low yield, is unjustified because of the great probability that silicon-carbon cleavage can occur under the experimental conditions.

Any interpretation of these experiment results should also recognize that Lewis acids interact with silazanes as follows:

$$\equiv Si\text{-}N= + M\text{-}X \longrightarrow \equiv Si\text{-}X + M\text{-}N=$$

Since many of the metal halides are tri- or tetrafunctional, cross-linked structures could result.

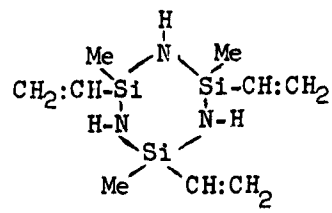
In a final experiment, the tetramer was heated without solvent in the presence of ammonium sulfate at 225-250°. Ammonia was evolved throughout the heating period, and 75 per cent of the starting material was recovered as a nonvolatile polymeric residue. The resulting polymer had a rather low molecular weight as indicated by an intrinsic viscosity in toluene of 0.045.

VI. THE PREPARATION OF MONOMERS AND INTERMEDIATES

New compounds, prepared and characterized during this report period, are summarized in Table III. Other compounds that were prepared are shown in Table IV.

Compound I was obtained directly from dichloromethylvinylsilane and ammonia.

$$Me(CH_2{:}CH)SiCl_2 + NH_3 \xrightarrow{C_6H_6}$$



(I)

Compounds II and III were prepared by treating dichloromethylvinylsilane with methylamine.

$$Me(CH_2{:}CH)SiCl_2 + MeNH_2 \xrightarrow[\text{ether}]{\text{petroleum}} Me(CH_2{:}CH)Si(NHMe)_2 +$$

(II)

$$MeN\left[SiMe(CH{:}CH_2)NHMe\right]$$

(III)

TABLE III

NEW COMPOUNDS

	Name	b.p. (°C)	$n_D^{(t)}$	Yield	Analyses N Calcd.	N Found	Si Calcd.	Si Found
I.	2,4,6-Trimethyl-2,4,6-trivinylcyclotrisilazane[a/]	120-23°/19 mm.	1.4779 (27°)	24-27	16.44	16.52	32.98	32.79
II.	Bis(methylamino)methylvinylsilane	65-5°	1.4318 (27°)	21	21.50	20.40 20.12 20.03	21.56	20.04 20.22
III.	1,3-Bis(methylamino)-1,3-divinyltrimethyltrisilazane	86°	1.4571 (24°)	11	18.31	18.11	24.48	24.66
IV.	Hexamethyl-1,3,5-trivinylcyclotrisilazane	110-13°/4 mm.	1.4783 (27°)	56	14.12	13.82	28.31	28.40
V.	p-Phenylenebis(dimethyl(methylamino)silane)	80-84°/0.3 mm.	1.5043 (28°)	37	11.10	10.91	22.25	22.02
					(C - Calcd., 57.07; Found 56.95 H - Calcd., 9.58; Found 9.73)			
VI.	p-Phenylenebis(dimethyl-n-butylaminosilane)	118-20°/0.07 mm.	1.4912 (28°)	6	8.32	8.15	16.69	16.52
					(C - Calcd., 64.21; Found, 63.91 H- Calcd., 10.78; Found 10.59)			

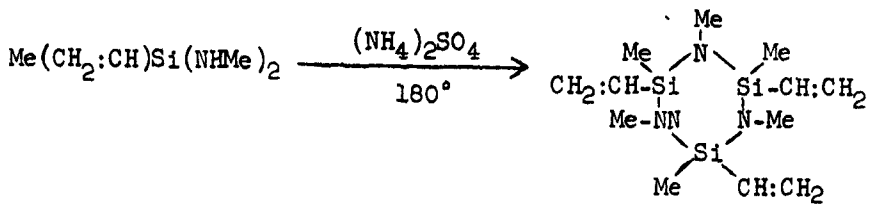
a/ $d^{27°} = 0.964$

TABLE IV

OTHER MONOMERS AND INTERMEDIATES

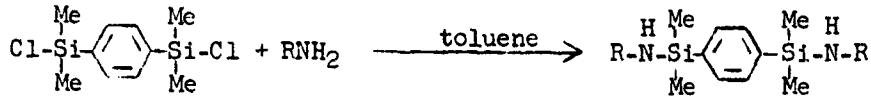
Name	b.p. (°C)	m.p. (°C)	$n_D^{(t)}$	Yield (%)	Reference
Hexamethylcyclotrisilazane	115-16°/86 mm.	-	1.4413 (27)	33-38	7
Octamethylcyclotrisilazane	-			26-41	7
Nonamethylcyclotrisilazane	96-7°/10 mm.	33.4°	-	80-89	Summary Report No. 1, p. 21
Hexamethyl-1,3,5-triphenyl-cyclotrisilazane	-	234-42°	-	20	8
Dimethylbis(methylamino)silane	107-108°	-	-	23-44	8
1,3-Bis(methylamino)pentamethyl-disilazane	78°/11 mm.	-	1.4393 (27°)	26-37	8
N-Trimethylsilylhexamethylcyclo-trisilazane (VIII)	112-13°/10 mm.	-	1.4596 (26°)	55-69	Summary Report No. 1, p. 18
N,N'-Bis(trimethylsilyl)hexa-methylcyclotrisilazane (IX)	122-3°/6 mm.	-	1.4396 (27°)	46	9
1,3-Bis(chlorodimethylsilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane	83-95°/0.1-0.4 mm.	-	-	65	Summary Report No. 1, p. 3
1,3-Bis(dimethyl-2,2-dimethylmethyl-aminosilyl)-1,3-diaza-2-silacyclo-pentane	76°/0.3-0.4 mm.	-	1.4585 (26°)	83	Summary Report No. 1, p. 3
p-Phenylenebis(chlorodimethylsilane)	108-10°/1.5 mm.	-	-	39	10

To obtain IV, II was heated to 180° in the presence of ammonium sulfate.



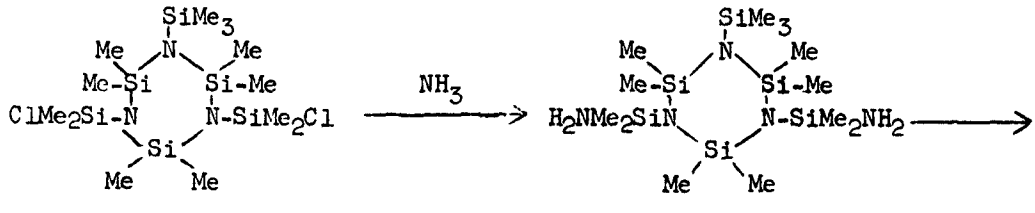
(IV)

V and VI were prepared by treating p-phenylenebis(chlorodimethylsilane) with the appropriate amine.

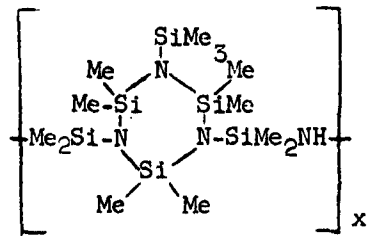


(V), R = Me; (VI), R = n-Bu

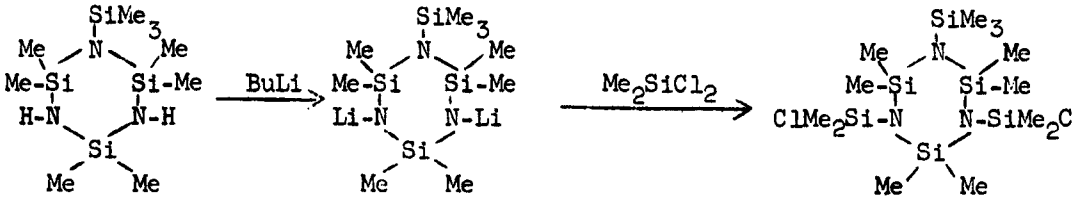
N-Silylated derivatives of hexamethylcyclotrisilazane are potentially useful intermediates in various polymerization reactions, either as monomers in condensations with organic diols or as intermediates in the preparation of other monomers. For example, ammonolysis of N,N'-bis(chlorodimethylsilyl)-N"-(trimethylsilyl)hexamethylcyclotrisilazane (VI) should give an intermediate useful in the following sequence:



(VI)



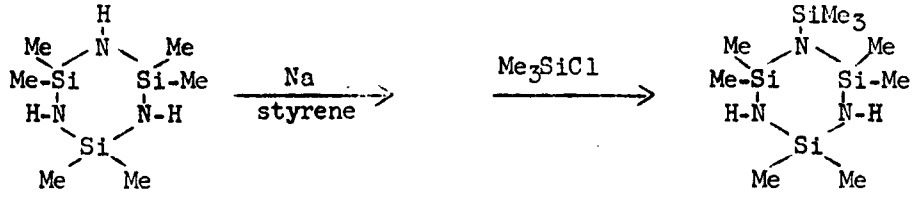
Attempts to prepare compound VI followed the method described in the literature for the preparation of other N-silylated cyclosilazanes.[9] The lithium salt of the cyclosilazane, prepared from the cyclosilazane and butyllithium, was heated with dichlorodimethylsilane at about 160° in an autoclave.



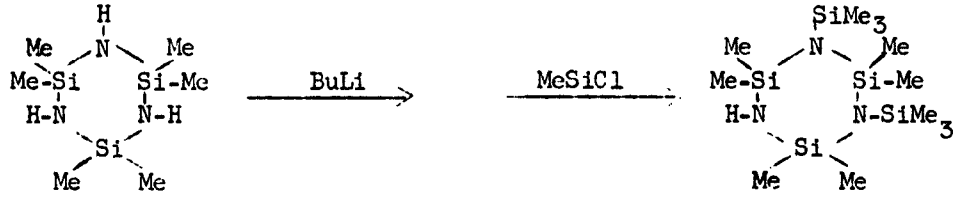
(VII)

This method of synthesis was investigated in a series of experiments in which minor variations in the preparative procedure were employed, but compound VI could not be isolated from any of the reaction products. Although stoichiometric quantities of lithium chloride and butane were formed, the products were complex mixtures, difficult to separate by distillation. Only low yields of materials in the expected boiling range of the desired product were obtained.

A method for preparing N-trimethylsilylhexamethylcyclotrisilazane (VIII) from the sodium intermediate was described in Summary Report No. 1, and the synthesis of N,N'-bis(trimethylsilyl)hexamethylcyclotrisilazane (IX) from the lithium intermediate has been described in the literature.[9]



(VIII)



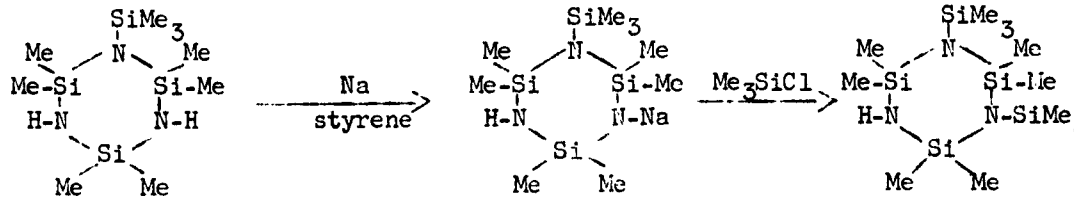
(IX)

In preparing quantities of VIII and IX for polymerization studies, it was found that the properties of IX agreed well with those reported in the literature. However, a comparison of the properties of IX with other members of the series of silylated cyclosilazanes revealed several anomalies. These properties are summarized in Table V, all properties except those of VIII being taken from the literature. The similarity in the vapor pressures of VIII and IX are surprising, and the refractive index of IX appears to be out-of-line with the rest of the series. The low refractive index is reflected in the poor agreement in the values for the calculated and experimental molar refraction.

Infrared spectra of hexamethylcyclotrisilazane, VIII, and IX (see Fig. 10) were consistent with the proposed structures for the three compounds. Of particular interest is a band at about 1030 $cm.^{-1}$, which is said to be characteristic of organosilyl-substituted cyclosilazanes.[9] This band was absent in hexamethylcyclotrisilazane, weak in VIII and strong in IX. The band at 840 $cm.^{-1}$ in the spectra of VIII and IX can be attributed to the presence of the trimethylsilyl group.

NMR spectra confirmed the structure of VIII, but were not consistent with the proposed structure of IX. Three peaks attributable to methyl protons were observed in VIII at -1.32, -1.38, and -1.45 ppm . (cyclohexane reference). The ratio of peak areas was 4.0:2.9:2.0 (calculated, 4.0:3.0:2.0). The spectrum of IX consisted of four bands at -1.26, -1.46, -1.48, and -1.51 ppm. (cyclohexane reference) with relative intensitites of 3.0:3.4:0.9:2.3, respectively. IX requires three peaks with relative intensities of 3.0:2.0:1.0.

Chemical evidence tended to confirm the structure of IX in that it could be prepared from VIII via the sodium intermediate.

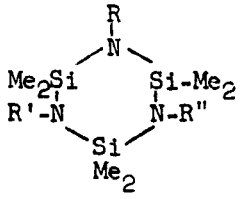


The product of this reaction was identical with the product obtained in the lithium reaction; however, the compound was obtained in a yield of only 20 per cent.

Although some data substantiate the reported structure of IX, there is sufficient evidence to indicate a structure other than that proposed in the literature. In view of this evidence, IX and related compounds have less value in the synthesis of polymers with known structures than originally anticipated.

TABLE V

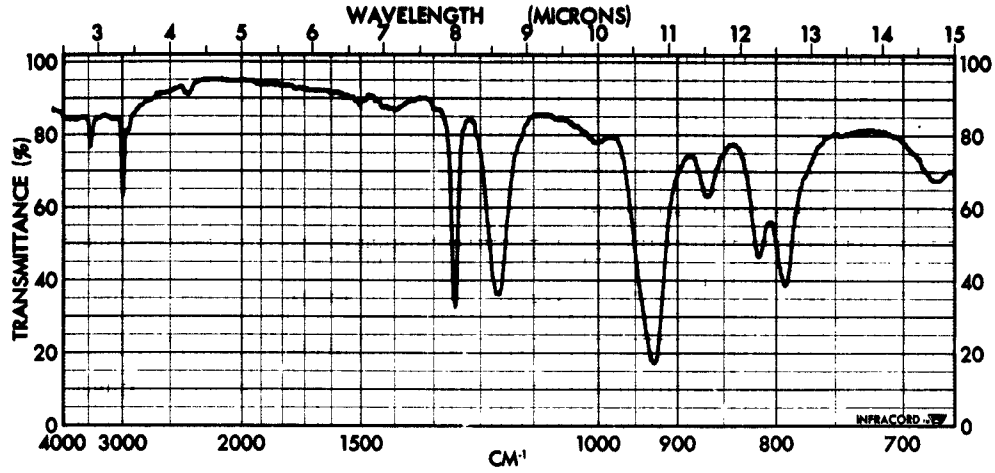
PROPERTIES OF HEXAMETHYLCYCLOTRISILAZANE AND ITS N-SUBSTITUTED TRIMETHYLSILYL DERIVATIVES



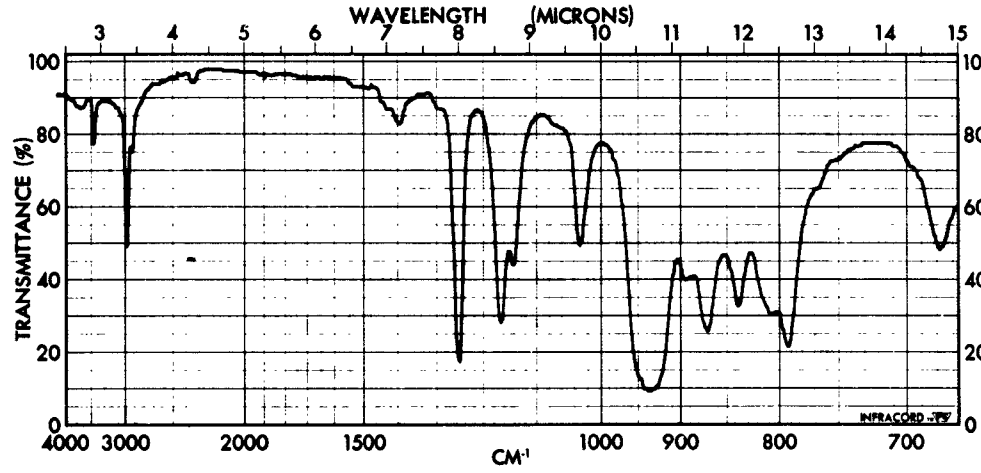
R = R' = R" = H
R = R' = H; R" = $SiMe_3$
R = H; R' = R" = $SiMe_3$
R = R' = R" = $SiMe_3$

	Boiling Point (°C/mm)		n_D^t	d^t	MR_D Calcd.[d]	MR_D Exptl.
Hexamethylcyclotrisilazane[a]	111-112°/85	188°/756	1.4448^{20}	0.9196^{20}	63.53	63.51
N-trimethylsilylhexamethylcyclotrisilazane	112-13°/10	255°/760[c]	1.4596^{26}	0.931^{27}	86.57	85.75
N,N'-bis(trimethylsilyl)hexamethylcyclotrisilazane[b]	81.0-81.7°/2	260°/760[c]	1.4420^{20}	0.973^{20}	109.62	98.95
N,N'N"-tris(trimethylsilyl)hexamethylcyclotrisilazane[b]	143-45°/0.09	333°/723[d]	1.4823^{20}	0.940^{20}	132.66	132.31

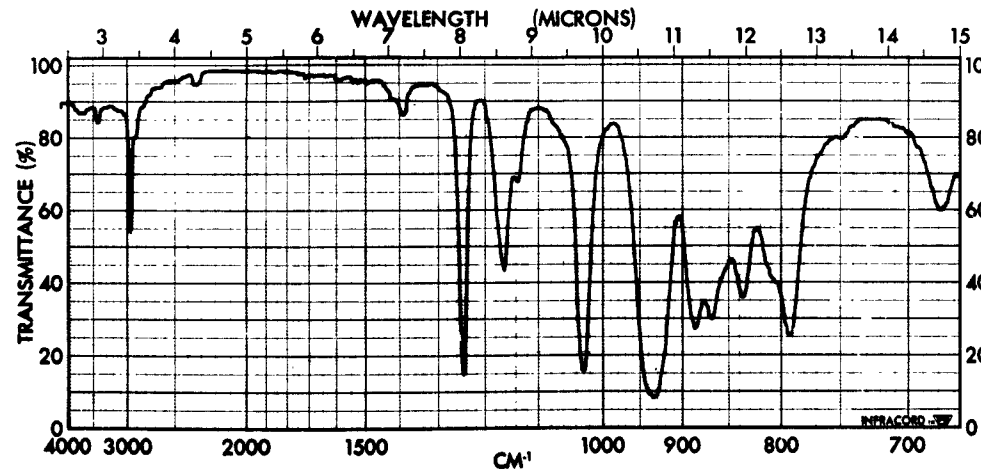
a/ Reference 7.
b/ Reference 9.
c/ Extrapolated.
d/ Reference 11.



Hexamethylcyclotrisilazane



N-Trimethylsilylhexamethylcyclotrisilazane



N,N'-bis(trimethylsilyl)hexamethylcyclotrisilazane

Fig. 10 - Infrared Spectra of Monomers

VII. FUTURE WORK

New work on polymers in the silicon-nitrogen series will include effort on all three phases outlined in the introduction to this report, but the chief emphasis will be placed on obtaining improved hydrolytic stabilities and finding satisfactory curing methods. In the synthesis of new polymers, attempts will be made to increase molecular weights into the range of 200,000 to 500,000.

Improvements in the hydrolytic stability of polymers will require structure modification of the polymers, and therefore, some effort will be required on the synthesis of new monomers.

For cross-linking studies, it is highly desirable that new polymers incorporate reactive groups on the polymer chain to provide vulcanization sites. Possible cross-linking methods include: Use of trihydroxy aromatic compounds which yield a free hydroxyl group useful for cross-linking with diisocyanates; incorporation of an acceptor atom, for example, boron, in the polymer chain; use of polyfunctional compounds containing silanic hydrogen to cross-link through silicon-attached vinyl groups; and the condensation of silylamine hydrogen with bifunctional isocyanates.

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